

Olivine Manganese Silicate as a New Cathode Material for Li-Ion Batteries

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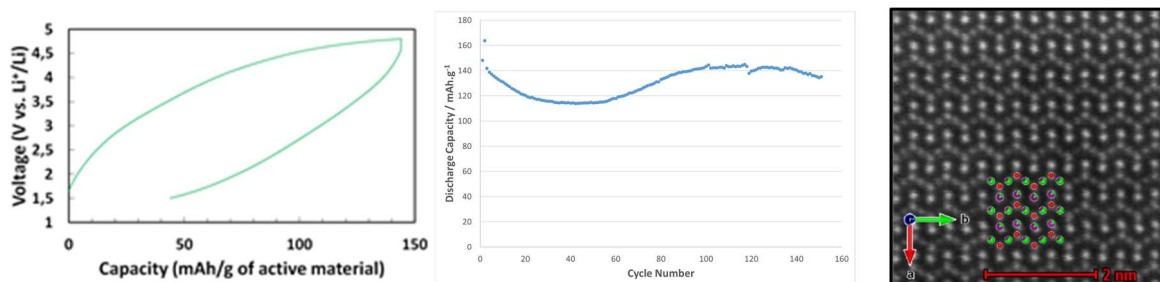
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Since the unveiling of LiFePO₄ by Padhi *et al.* in 1997 [1], polyanionic materials attracted a great part of the research effort in the scientific community. However, LFP cannot compete with layered oxides for energy density and alternatives like silicates Li₂MSiO₄ (M=Fe, Mn, Co, Ni) are studied due to a theoretical capacity of 333mAh.g⁻¹. Contrary to Li₂FeSiO₄, the two Li⁺ of the manganese compounds are supposed to be extracted below the degradation limit of common electrolytes [2,3]. However, due to the instability of manganese ions in original tetrahedral environments, an amorphization process takes place during extraction of lithium and leads to irreversible structural distortions and capacity fading [3].

This study focuses on manganese silicates with Mn in octahedral environment. Olivine MgMnSiO₄ is of particular interest since it has the same olivine structure than LFP and has already been considered as a cathode material for Mg batteries [4] and replacing Mg by Li in MgMnSiO₄ would lead to LiMnSiO₄. This lithiated olivine silicate has never been synthesized in the literature but DFT calculations showed structural stability and a theoretical electrochemical activity above 4 V vs. Li⁺/Li for the Mn³⁺/Mn⁴⁺ redox couple [5,6].

The preparation of MgMnSiO₄/ composites by a sol-gel process and their electrochemical activity in Lithium cells will be discussed here in details. We will present the effect of the synthesis conditions for the exchange of Mg by Li (such as chemical oxidation by NO₂BF₄, or molten salt synthesis), and we will also discuss the effect of the antisite ratio, a parameter of first importance to obtain a good reversible capacity. This optimization work allowed us obtaining a stable capacity of 140mAh.g⁻¹ over more than 150 cycles without modification of the olivine structure. A detailed electrochemical analysis will also be presented. Finally, we will make an opening towards new mixed silicate compounds unreported in the literature.



Left and Center: Cycling behavior of Olivine Manganese Silicate Material at C/5 rate

Right: HR-STEM confirming the olivine structure of the active material

References:

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